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Silicon minority-carrier lifetime degradation during molecular beam heteroepitaxial III-V material growth

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Abstract

A major hindrance to the development of devices integrating III-V materials on silicon, where it is an active component of the device, is the preservation of its electronic quality. In this contribution, we report on our effort to identify the mechanism behind the severe decrease in the bulk minority-carrier lifetime of silicon after heteroepitaxial growth of gallium phosphide, in our molecular beam epitaxy (MBE) system. We identify that the drop in lifetime occurs at a threshold temperature of 500°C; we assign the increased recombination rate to extrinsic, fast-diffusing impurities coming from the MBE chamber environment. Impurities can be gettered by phosphorous diffusion, leading to a lifetime recovery. Moreover, we narrow the list of contaminants based on specific experimental observations and compare our hypothesis to modeling of injection-dependent lifetime spectra. Finally we show that coating the silicon wafer with a sacrificial silicon nitride film helps significantly to reduce contamination and provides a path to successful III-V growth on silicon.

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Keywords: crystalline silicon solar cells; III-V material; minority-carrier lifetime degradation; carrier-selective contact; gallium phosphide.

1. Introduction

Integrating III-V materials heteroepitaxially grown on Si has great potential to advance future solar cells

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efficiency, through the development of all-III-V multi-junctions cells on a relatively inexpensive substrate, tandem or multi-junction cells with a Si bottom-cell monolithically integrated, or by using the III-V as a carrier-selective contact material for Si single-junction cell [1–3]. The last two approaches require that the electronic properties in the Si must not be altered to reach high performance. However, degradation of Si bulk minority-carrier lifetime was recently reported by groups growing III-V materials using different techniques such as metalorganic vapor phase epitaxy (MOVPE) or metalorganic chemical vapor deposition (MOCVD) [3–5]. We report here a similar degradation effect for the case of gallium phosphide (GaP) grown on Si by molecular beam epitaxy (MBE). This degradation is a major hindrance in the development of any devices with Si active material and calls for a more generalized understanding of the underlying mechanism and solutions to circumvent the issue. We present results of our investigation on the nature and origin of this potentially catastrophic minority-carrier lifetime degradation for the case of MBE growth.

2. Experimental

Float-zone (FZ) n- and p-type (100) double-side-polished, 1–5 Ω·cm, 280-µm-thick Si wafers were used for our experiments. III-V materials growth is performed in a solid-source Veeco GEN-III MBE system, with typical base and process pressures in the mid-10^{-10} and mid-10^{-8} Torr, respectively. Samples loading involves several degassing steps at 380°C and 240°C in the growth chamber; then the temperature is elevated to 800°C for surface de-oxidation. The GaP growth itself occurs at 400–500°C, from Ga and P_2 source cells (Fig. 1). Annealing tests reproducing growth conditions were performed between 450–800°C, for 30 min. Samples were initially cleaned in RCA solution and dipped in 5% diluted hydrofluoric acid (HF) to remove the native oxide. After annealing or GaP growth, samples were etched in a mixture of nitric, acetic and HF acid solutions (HNA) to remove ~ 5–100 µm of material of each side (and the GaP film); this step allows to eliminate contaminants that would accumulate at the surface. After cleaning (RCA, HF), the surface was passivated with 50 nm intrinsic hydrogenated amorphous silicon (a-Si:H) by plasma-enhanced chemical vapour deposition. This resulted in a surface recombination velocity lower than 5 cm/s; we considered this value low enough to assume that the measured effective minority-carrier lifetime is equivalent to the bulk lifetime. For the gettering process, the passivation layer was removed by HNA etching and samples were exposed to oxygen and $POCl_3$, at 830°C in a diffusion furnace, with 25 min drive in step. Finally, the phosphorus glass and emitter region were etched, surface cleaned and a-Si:H passivated. Minority-carrier lifetimes were evaluated by photoconductance decay injection- and temperature-dependent measurements, on a Sinton lifetime tester.

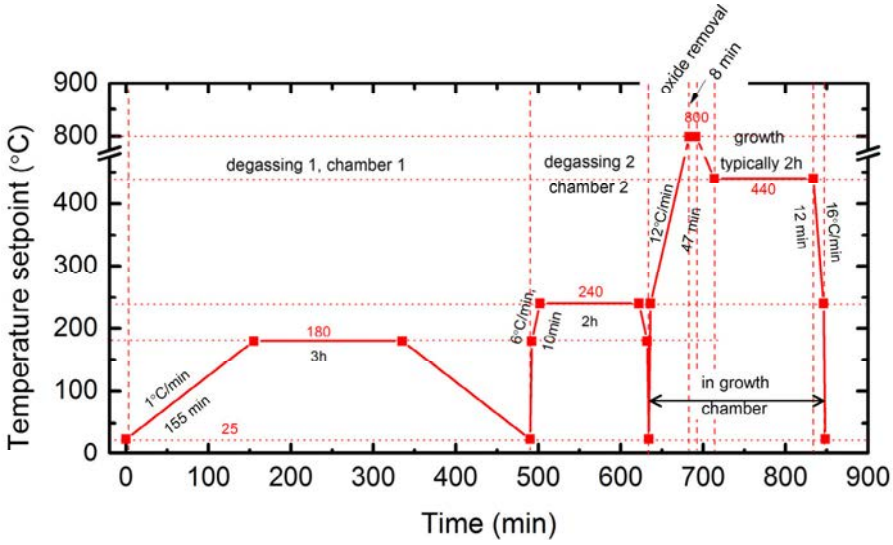

Fig. 1. Typical temperature-time profile of MBE GaP growth processes.

3. Results and discussions

3.1. Experimental observations

Our typical GaP heteroepitaxial growth process starts by heating the silicon over 800°C to get rid of any oxygen monolayer still present on the surface, whereas the GaP growth itself takes place between 400–500°C. Preliminary tests showed that after etching the GaP, FZ Si wafers are characterized by a severe minority-carrier lifetime drop from initially milliseconds range (with a 50-nm-thick (i) a-Si:H coating on both sides) to less than 100 µs. A similar bulk minority-carrier lifetime degradation was reproduced by annealing bare Si wafers in the MBE chamber. As shown in Fig. 2, the effective lifetime was still as high as the reference one after 450°C annealing, but decreased from the ms to the low µs range for 600°C and 800°C annealing. The actual threshold was identified at 500°C. Conversely, Si wafers heated in a rapid-thermal-processing furnace to similar temperature did not exhibit any major degradation. This indicates that the lifetime degradation is not strictly due to the GaP growth or from the GaP/Si interface recombination, but rather coming from the MBE.

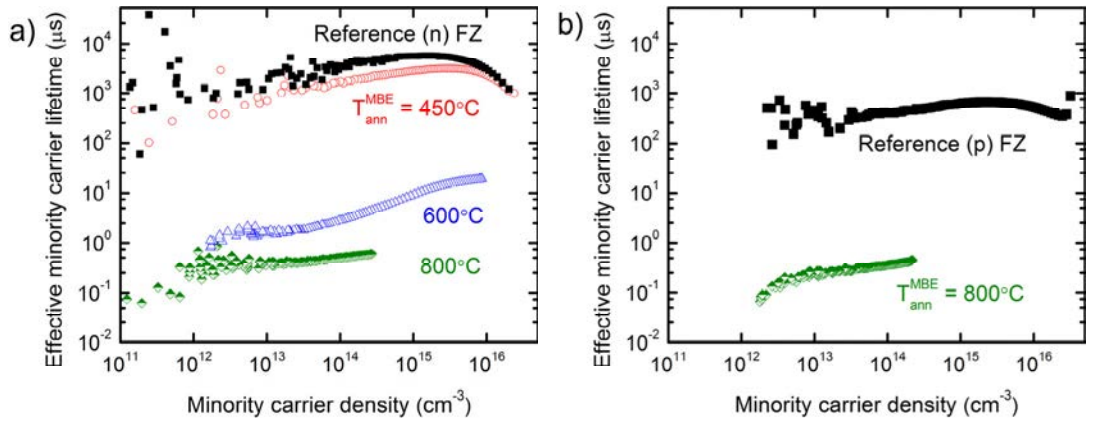

Fig. 2. Injection-dependence of the effective minority-carrier lifetime of a) FZ n-type and b) FZ p-type wafers, before and after annealing at different temperatures in the MBE chamber.

The same n-type FZ Si samples were then exposed to phosphorous diffusion from a $POCl_3$ source, to getter the impurities. This resulted in a recovery of the effective lifetime to values above 1 ms for all samples (Fig. 3). The effectivity of the gettering suggests that the lifetime degradation originates from highly mobile and highly recombination active impurities diffusing from the MBE chamber. Contrarily to gettering, annealing the degraded samples at similar temperature in the diffusion oven without a phosphorous source, or in a rapid-thermal-processing furnace (not shown), did not lead to significant lifetime improvement (Fig. 3). This seems to confirm that the recovery is mostly related to the segregation of impurities to the phosphorous-rich emitter or glass region, and is not linked to the annealing of intrinsic crystal defects. Interestingly similar observations and conclusions were reported in the case of GaP grown on Si by MOCVD by Varache *et al.* and potentially when using MOVPE by Garcia-Tabares *et al.* [3–5]. Though there is no evidence that the lifetime degradation be caused by the same impurity, the similarity of the faced issue seems to indicate a contamination that can be present probably in trace concentration in the growth chamber, without harming the III-V material performance itself. This only highlights the sensitivity of Si electronic quality to contamination and importance of improving our control over high-temperature processes involved during III-V growth.

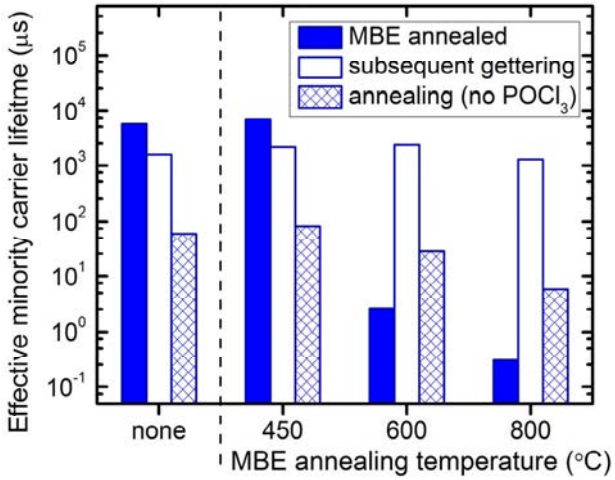

Fig 3. Evolution of the effective minority-carrier lifetime of the MBE-annealed n-type FZ wafers, after the indicated treatment (at an injection level of 1x1015 cm-3, except for the 800°C annealed samples at 1x1014 cm-3).

We then conducted additional experiments and our observations and considerations contribute to the establishment of a list of possible contaminants:

- A similar trend in lifetime drop was observed for CZ and FZ wafers, both n- and p-type. This suggests that the defects are not complexes associated with O or C contaminants in CZ wafers, or linked to a specific dopant. Moreover, no oxygen interstitial signature was detected in the FZ wafers, prior- or post-annealing by Fourier-transform infrared spectroscopy.
- V, Ti and Ta are very detrimental to the lifetime at ultra-low concentration, but are slow diffusers, which should make them impervious to gettering, contradicting our observation [8]-[9].
- Fe, Cr and Mn are moderate-fast diffusers and well-known to form pairs with charged ionized dopant atoms [8]. In our investigation no change in lifetime for the p-type FZ Si was seen after illumination, therefore Fe, Cr and Mn are excluded from the list.
- The wafer holder is made of Mo, which is categorized as a medium-fast-diffusing metal and some gettering effect has been reported [9]–[10].
- Ni, Cu, Co and their complexes, are known to form several different highly active defect levels, and to precipitate upon cooling of the wafer. Despite etching of the wafer surfaces, these can still be detrimental at relatively low concentrations. [6]–[7]–[11].
- Finally, Au, Ag and Zn are all known to form deep levels in the Si band gap, but Ag and Zn do not respond well to gettering. Au is moreover an amphoteric defect, which would explain the degradation effect seen in both n-and p-type Si [11].

3.2. Fitting of IDLS data

Based on these observations, we evaluated different impurities candidates by fitting our injection-dependent effective lifetime spectra (IDLS) using reported defect parameters (capture cross-sections and energy level). We assumed Shockley-Read-Hall (S-R-H) statistics, which describes the lifetime governed by recombination through defects τ_{SRH} as (here for p-type silicon):

$$\tau_{SRH} = \frac{\tau_{n0}(N_A + p_1 + \Delta n) + \tau_{p0}(n_1 + \Delta n)}{N_A + \Delta n}$$

where N_A is the doping acceptor concentration, and Δn the excess minority carrier density, *i.e.* electrons. The electron- and hole-capture time constants τ_{n0} and τ_{p0} are related to the defect density N_t, the thermal velocity v_{th} and the electron- and hole-capture cross-sections σ_n and σ_h via:

$$\tau_{p0} = 1/N_t\sigma_p v_{th},$$
$$\tau_{n0} = 1/N_t\sigma_n v_{th}$$

Finally, the densities n_1 and p_1 equal the equilibrium electron and hole densities when the defect energy level E_t coincides with the Fermi level:

$$p_1 = N_v exp\left(-\frac{E_t - E_v}{kT}\right) n_1 = N_c exp\left(-\frac{E_c - E_t}{kT}\right)$$

The fitting is performed by keeping E_t, σ_n and σ_h constant, while varying N_t; we considered that, even if different impurities might be present, only one most-detrimental defect controls the effective lifetime. We also assumed a homogeneous distribution of the contaminant throughout the wafer thickness, based on observations that the effective lifetime of samples annealed at 600 and 800°C did not change after etching ~ 100 µm material from each surface.

Fig. 4 shows the best results obtained for Au and Mo defects [8]–[9], compared to the experimental IDLS curves for n-type FZ Si annealed at 600°C and p-type FZ Si annealed at 800°C. Ni, Cu and Co were not included, since they can take many different deep defects energy levels of unclear capture cross-sections, which can be considered as forming a defect band. As seen in Fig.4 the fit for Mo is not conclusive, which suggests that it is not the main culprit. Conversely, Au resulted in good match with the effective IDLS data, for n- and p-type FZ Si. These also seem to match the activation energy $E_t = E_v - 0.315$ eV, extracted from preliminary temperature- and injection-dependent lifetime measurements in n-type Si (not shown), but will need to be complemented by additional characterization, such as deep-level transient spectroscopy that shall bring insight in the nature of the metal impurities in terms of its energy level in the band gap and the majority-carrier capture cross-section.

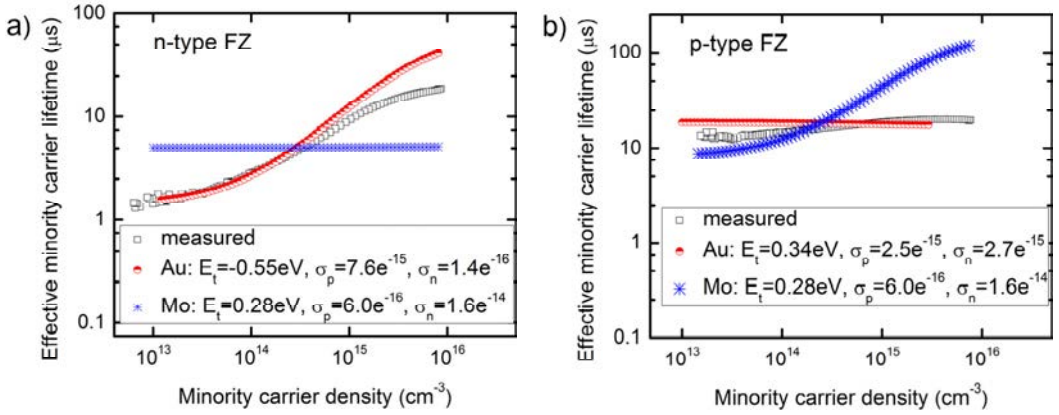

Fig. 4. Fitting of the injection-dependent lifetime curves for (a) n-type FZ Si annealed at 600°C and (b) p-type FZ Si, annealed at 800°C, implementing S-R-H recombination for Mo and Au literature defect parameters [8]–[9].

3.3. Defect engineering - containing impurities to a sacrificial sink

The above-described experiments however do not allow to identify and eliminate the particular piece in the MBE chamber that is the source of contaminant. Instead of trying to solve this needle-in-a-haystack problem, we choose the approach to contain the contamination by forcing impurities to concentrate at a sacrificial interface and preventing them from diffusing in the whole wafer. To do so, we coated the Si wafer with silicon nitride (a-SiNx:H) by PECVD before annealing or GaP growth. After etching the SiNx plus ~ 5 μm of Si (and GaP if present) and surface passivation, we measured a bulk lifetime preserved in the ms-range. A similar lifetime was measured if coating both sides or the back-side of the wafer, which tends to indicate that contamination is originating from the sample holder.

Our final purpose being the preparation of heterojunction Si solar cell using a thin GaP layer as a carrier-selective contact and not a p-n junction, we cannot take advantage of the phosphorous diffusion step that would combine gettering of impurities and emitter (or P-rich if starting from an n-type) formation, like has been shown in [3] (using phosphine as P-source). We could alternatively formed a P-rich region at the back of the Si, grow GaP and etch away the back side; this approach is however more constraining than the one using a PECVD SiNx film.

4. Conclusions

This contribution presents the results of our investigations regarding the origin of the severe degradation of the minority-carrier lifetime of FZ Si wafers after III-V growth in our MBE chamber. We find that highly-mobile impurities from the MBE system diffuse in the Si during high-temperature processes, forming highly-active recombination centres. These can be post-process-gettered by phosphorous diffusion, leading to a recovery to almost initial lifetime values. Alternatively a way to circumvent the bulk contamination is proposed by offering a sacrificial interface at which impurities can be contained and removed by etching; this opens now the path to our work of development of GaP carrier-selective contacts.

Though the exact nature of the contamination is still to be elucidated, fitting of IDLS and TIDLS provides a tool to evaluate the signature—range of energy level and capture cross-section—of the most detrimental defect, which will be further refined to go beyond fitting reported literature defect parameters. Also, we think that identification of the type of impurity provides opportunity for minimizing of the impact of the contamination via optimization of the MBE thermal budget, as the concentration, location and precipitate formation of the impurity depend on its diffusivity and solubility, but more importantly is determined by the temperature-time profile of the annealing or growth steps.

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